Short Communication

Analysis of ε-caprolactam and its cyclic oligomers by high-performance liquid chromatography

Luisa Bonifaci, Donatella Frezzotti, Gianfranco Cavalca, Edgardo Malaguti and Gian Paolo Ravanetti*

Enichem Polimeri, Mantua Research Centre, Via G. Taliercio 14, 46100 Mantua (Italy)

ABSTRACT

A high-performance liquid chromatographic method for the determination of ε-caprolactam and its cyclic oligomers is presented. The method uses a methanol–water mixture as eluent. The separation of peaks is well defined and their quantitative determination is performed by calibration with known purity standards. By comparing the ultraviolet and refractive index detection responses, a disagreement with the reported data regarding ε-caprolactam dimer and trimer extinction coefficients was observed and the tetramer and pentamer extinction coefficients were estimated.

INTRODUCTION

The problem of separation of ε-caprolactam cyclic oligomers has existed since the early 1950s. The reported methods use fractional sublimation [1], paper chromatography [2], gas chromatography [3] and gel permeation chromatography [4]. Although suitable, all of them have some limitations of application due to either the substances' nature (higher oligomers are not sublimable) or the analysis length or the low resolution.

Most recently, the introduction of high-performance liquid chromatography (HPLC) has brought an appreciable improvement in ε-caprolactam oligomer analysis, since a large range of efficient columns are available and there is a choice of pure solvents and mixtures.

Krajnik *et al.* [5] proposed the use of reversed-phase (RP)-HPLC on C_{18}-type columns and a methanol–aqueous acetic acid (30:70) mixture as

eluent and obtained a good separation between the dimer and the monomer, the most critical point of the whole analysis.

With the same type of columns, but using a methanol–water (35:65) mixture, Tai and Tagawa [6] succeeded in obtaining good separation of higher oligomers, but failed in the dimer–monomer separation.

Guaita [7], using an RF-8 5-μm column and a trifluoroethanol–water (40:60) mixture at 50°C, obtained a good separation of ε-caprolactam cyclic oligomers up to decamer. All these authors used UV detection at a wavelength at which the eluent absorption is negligible (typically 205 or 210 nm).

The method presented in this paper uses a reversed-phase C_{18}-type column and a methanol–water 40:60) mixture as eluent at 25°C. This technique is very efficient for dimer–monomer separation and allows the quantitative determination of oligomers, without using fluorinated solvents.

EXPERIMENTAL

Equipment

The HPLC analyses were performed using a GPC-ALC 150C Waters chromatograph equipped with a differential refractive index (RI) detector and a UV detector (Waters Model 490) at 210 nm.

A Spherisorb RP-18 Phase Sep (25 cm × 4.6 mm I.D.) column and a methanol–water (40:60) mixture at 25°C as eluent were used. The solvent flow-rate was 0.5 ml/min; the sample concentration and the injected volume were 0.01% (w/v) and 20 μl, respectively.

Materials

For the calibration curves of the UV and RI detectors, ε-caprolactam, dried in a vacuum oven at 40°C for 120 h, and nine fractions of cyclic dimer and trimer obtained from fractional sublimation of a oligomer mixture were used. All the products were supplied by the Enichem nylon 6 industrial plant (Porto Marghera, Italy). The same mixture was successively characterized by HPLC after ethanol extraction.

In order to obtain standard samples of dimer and trimer, fractional sublimation according to Heikens [1] was used. The compositions of the obtained fractions were evaluated by HPLC. The purity of the standard fractions used for the calibrations ranged between 96.7 and 94.7% for the dimer and between 97.5 and 98.5% for the trimer.

RESULTS AND DISCUSSION

The HPLC experimental conditions chosen in the present paper afford a good separation of the cyclic oligomers of ε-caprolactam, especially of the dimer. We also found, as previously reported [5–7], that the dimer is eluted before the monomer. Figs. 1 and 2 show the results of separation for both detectors. The retention times measured by the UV detector were: ε-caprolactam, 11.75 min; dimer, 11.00 min; trimer, 17.37 min; tetramer, 31.25 min; pentamer, 60.63 min. The analysed mixture did not appear to have higher oligomers.

For the quantitative analysis of the chromatographic peaks, the calibration curves of monomer, dimer and trimer for both detectors were determined. All the curves are linear with regression correlation coefficients higher than 0.995.
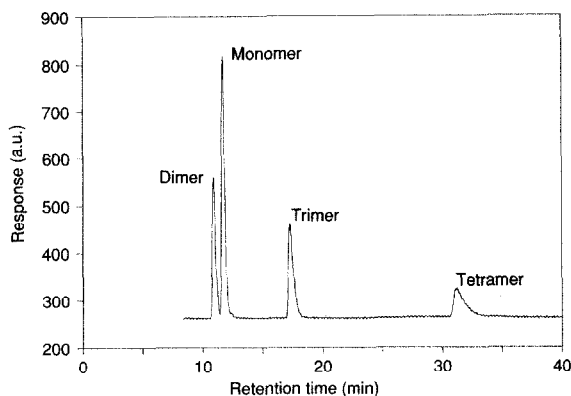

Fig. 1. UV chromatogram of oligomer mixture (pentamer is omitted for clarity).

With RI detection, the dimer and the trimer have a single calibration curve which was used also for the determination of tetramer and pentamer. Fig. 3 shows this curve together with the ε-caprolactam one.

With UV detection each component has its own calibration curve (Fig. 4). Contrary to what was expected on the basis of the extinction coefficient values at 210 nm [4,8], the dimer appears to have a lower response than the trimer. This finding is also strengthened by the fact that the ratios of the UV to RI peak areas are systematically lower for the dimer in all the samples.
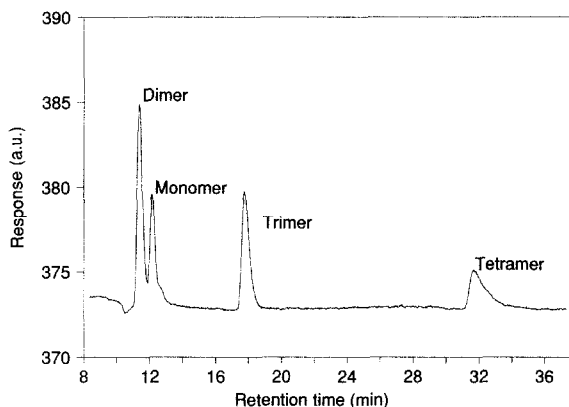

Fig. 2. RI chromatogram of oligomer mixture (pentamer is omitted for clarity).
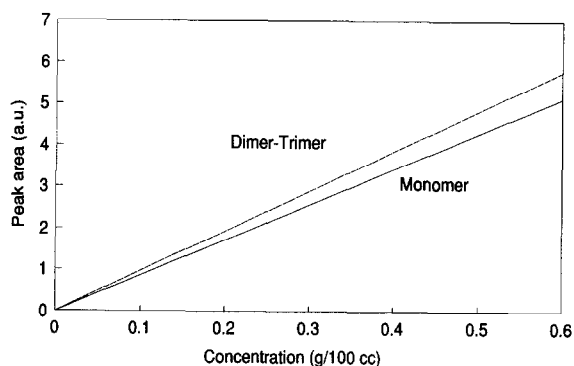
Fig. 3. RI calibration of ε-caprolactam, dimer and trimer.

TABLE I

EXTINCTION COEFFICIENTS OF ε-CAPROLACTAM AND ITS CYCLIC OLIGOMERS AT $\lambda = 210$ nm

Compound	ε (l/mol repeating unit · cm)			
	Calculated	Experimental	Ref. 8	Ref. 4
ε-Caprolactam		3160	3325	2800
Dimer	1080	900	1070	980
Trimer	1170	1060	970	970
Tetramer	1100		970	970
Pentamer	1130		970	970

Spectrophotometric measures at 210 nm on these samples have confirmed the above observations. As shown in Table I, in which the extinction coefficient values are reported, there is clearly a lack of agreement with the literature data. Also shown in Table I are the extinction coefficient values calculated from the previously determined calibration curves. The agreement between the spectrophotometric and calculated data can be regarded as satisfactory, mainly for their trend.

Finally, for the determination of tetramer and pentamer via UV, the extinction coefficients from Table I and the ε-caprolactam calibration as reference were used.

An estimation of extinction coefficient values of tetramer and pentamer was attempted, by taking as a reference ε-caprolactam and the calibration curves previously determined. For both compounds a value of about 1100 l/mol · cm was obtained,
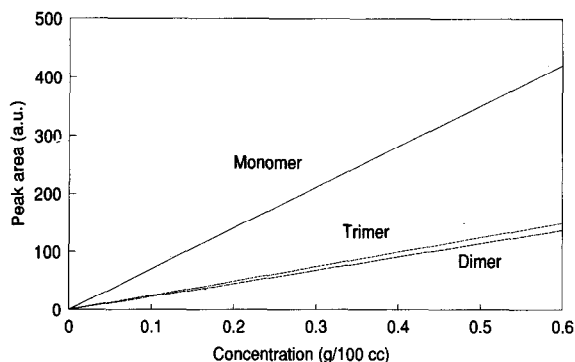
higher than those previously reported (970 l/mol · cm) [4,8]. Experimental confirmation of the calculated values was not attempted, since pure tetramer and pentamer were unavailable.

The use of the dual detection (UV and RI) allows a direct comparison of the determinations of the component concentrations in the mixture. The agreement between the data is satisfactory, therefore differential refractive index detection can be fruitfully used for such analyses, although no example of its use has been reported in the literature. Moreover, in our particular case, RI detection allowed us to verify the extinction coefficient values for dimer and trimer.

CONCLUSION

The proposed HPLC method is effective in the determination of the cyclic oligomers of ε-caprolactam, allowing a good separation between monomer and dimer. Differential refractive index detection appears to be as reliable as the UV detection using the reported experimental conditions. By comparing the UV and RI detector responses, some disagreement with the reported data regarding the extinction coefficients at 210 for dimer and trimer was found.

Fig. 4. UV calibration of ε-caprolactam, dimer and trimer.

REFERENCES

1 D. Heikens, *Rec. Trav. Chim. Pays-Bas*, 75 (1956) 1199.
2 M. Rothe, *Makromol. Chem.*, 35 (1960) 183.
3 J. M. Andrews, F. R. Jones and J. A. Semlyen, *Polymer*, 15 (1974) 420.
4 S. Mori and T. Takeuchi, *J. Chromatogr.*, 49 (1970) 230.
5 V. Krajnik, P. Bozek, J. Kondelikova and J. Kralicek, *J. Chromatogr.*, 240 (1982) 539.
6 K. Tai and T. Tagawa, *J. Appl. Polym. Sci.*, 27 (1982) 2791.
7 C. Guaita, *Makromol. Chem.*, 185 (1984) 459.
8 S. Russo, *La Chimica e l'Industria*, 63 (1981) 412.